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A HIGH-TEMPERATURE
ENGINEERING CERAMIC (Si_3N_4) BY
POWDER METALLURGICAL METHODS

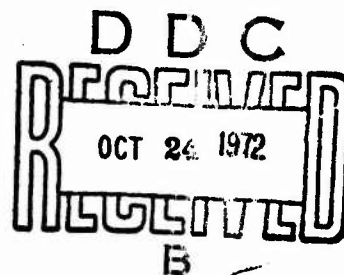
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CERAMICS DIVISION

June 1972

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Monograph by

MICHAEL W. LINDLEY* and R. NATHAN KATZ

June 1972

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A HIGH-TEMPERATURE ENGINEERING CERAMIC (Si_3N_4) BY POWDER METALLURGICAL METHODS

ABSTRACT

Silicon nitride has become a major structural ceramic material in the past decade. One form of this material, referred to as reaction-bonded silicon nitride, is of particular interest because it permits the production of ceramic components requiring little or no machining. This review discusses the application of powder metallurgical techniques to the fabrication of reaction-bonded silicon nitride, the nitridation process, and resultant properties.

Silicon nitride (Si_3N_4) has been seriously investigated and used as an engineering material in the last few years. The material is produced in two principal forms: hot-pressed¹ and reaction-bonded.^{2,3} Reaction-bonded silicon nitride in essence is not a single material but encompasses a spectrum of materials (like steel) with various property characteristics, and with an ability to be fabricated by differing processing techniques. The wide range of properties available to the designer/engineer results from these varied fabrication methods and subsequent processing conditions. Both forms of Si_3N_4 exhibit exceptionally good thermal shock resistance for a ceramic material, relatively good oxidation resistance, and good erosion/corrosion resistance.⁴ These properties have lead to consideration of silicon nitride ceramics for applications such as gas turbine combustors, rotors and stators,⁵ missile heatshields and nozzles,⁶ gas bearings and furnace components.

While the highest strength silicon nitride is produced by hot-pressing techniques, this brief review will limit itself to the discussion of reaction-bonded silicon nitride. It is most appropriate to discuss reaction-bonded Si_3N_4 (RBSi₃N₄) at a conference on powder metallurgy, since this unique material represents a true interface where the technologies of powder metallurgy and ceramics merge. Reaction-bonded silicon nitride is made by producing a preform of silicon metal powder by any one of several techniques (isostatic compaction, flame spraying, slip casting, or injection molding with a polymeric carrier). A replica of a complex-shaped silicon metal gas turbine combustor, fabricated by the flame-spray technique, is shown in Figure 1. The porous silicon metal compact is then reacted in an atmosphere of nitrogen and RBSi₃N₄ results. Thus the ceramist literally does powder metallurgy up to the point of sintering and then instead of sintering in a neutral atmosphere, reacts the metal powder with the atmosphere during the firing stage to produce a ceramic. The several truly unique aspects of both the reaction bonding process and the material which results will be discussed below.

The unique aspect of the reaction bonding process in silicon nitride is that the dimensions of the original silicon metal preform are preserved to within 0.1%.



Figure 1. FLAME-SPRAYED SILICON METAL GAS TURBINE COMBUSTOR, PRIOR TO NITRIDATION. (Photo Courtesy of Admiralty Materials Laboratory)

This means in practice that complex shapes can be machined from a "green" silicon compact or more preferably a lightly reacted compact (10% nitrogen uptake), known as "bisque-fired" material. Such machinable compacts can be worked with conventional steel tools. Most flame-sprayed or molded silicon shapes require essentially no machining (although the as-sprayed silicon piece is usually robust enough to be machined without the need for an initial nitrogen firing). Since the fully nitrided piece preserves the dimensions of its precursor, costly machining of hard ceramic components is eliminated.

When silicon reacts with nitrogen to produce RBSi_3N_4 , a 23% volume increase results. To accommodate this volume increase with only 0.1% gross dimensional change requires that a substantial portion of the Si_3N_4 be formed in the void space. In fact, as will be shown below, the first Si_3N_4 to form occurs by whisker, platelet, or other intravoids growth of Si_3N_4 . Since the attainment of a homogeneous piece of Si_3N_4 requires that nitrogen gas have access to all volume elements of the body, a continuously connected pore network is required. To insure connectivity of a second phase in a microstructure, $15 \pm 3 \text{ vol\%}$ of second phase (in this case pores)^{7,8} is required. In practice, a silicon compact of about 60% green density yields an RBSi_3N_4 compact of about 75 to 77% density. Although high green densities and resulting high RBSi_3N_4 densities can be achieved in the flame-spray deposition process, the highest green densities (excess of $1.9 \times 10^3 \text{ kg/m}^3$ silicon green density) cannot be fully utilized since insufficient pore connectivity precludes totally reacting the silicon matrix. Silicon nitride occurs in two crystallographic forms: $\alpha \text{ Si}_3\text{N}_4$ (actually an oxynitride $\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$) and $\beta \text{ Si}_3\text{N}_4$, both of which are hexagonal.^{9,10} The α form apparently occurs first at low temperatures (high O_2 potentials)⁹ and starts filling the void space. This occurs at nitriding temperatures ranging between 1100 and 1400 C, and is illustrated schematically on the typical nitriding sequence shown in Figure 2. At the next stage of the nitriding sequence the silicon metal is taken above its melting point and reacts with nitrogen to form both β and also $\alpha \text{ Si}_3\text{N}_4$. The compact retains its structural integrity in the presence of liquid silicon metal because of the skeleton of $\alpha \text{ Si}_3\text{N}_4$ which has been formed. An alternate hypothesis of buckling and exfoliation of $\alpha \text{ Si}_3\text{N}_4$ films below the melting point of silicon can also account for this duplex structure which is shown in Figure 3.¹⁰

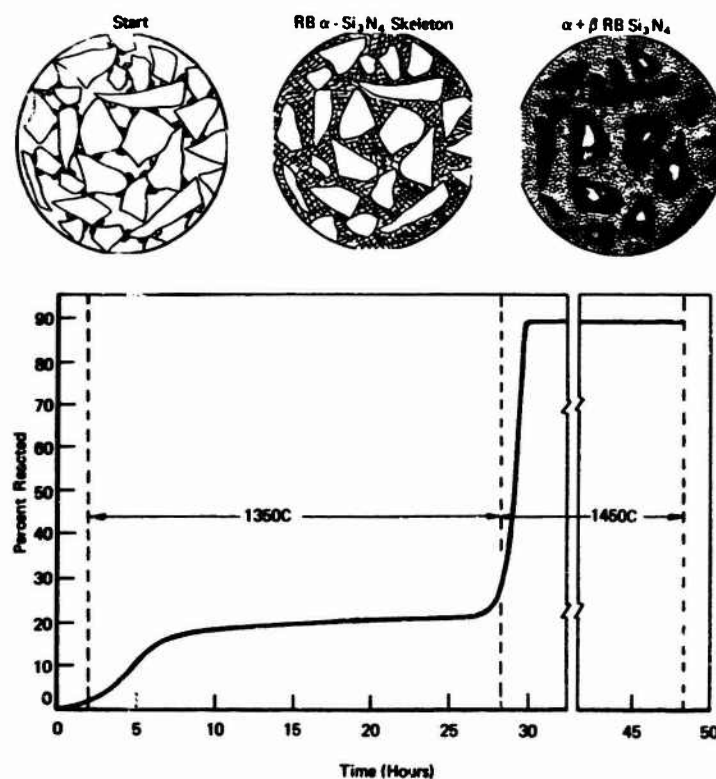
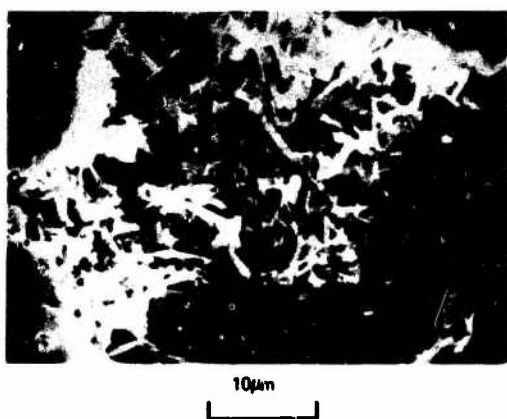
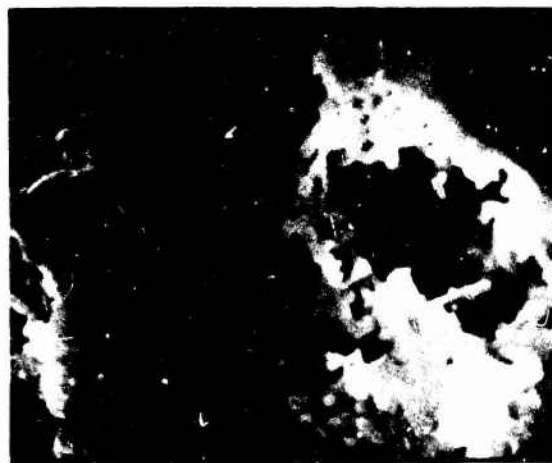


Figure 2. SCHEMATIC OF THE REACTION BONDING PROCESS AS A FUNCTION OF TIME AND TEMPERATURE. THE ILLUSTRATIONS AT THE TOP REPRESENT THE MICROSTRUCTURE DEVELOPMENT AT APPROXIMATE POSITIONS ALONG THE NITRIDATION CURVE.

19-066-1274/AMC-71



a. Cold-pressed and reaction-bonded material from Messier & Wong (Ref. 11). Mag. 1500X



b. Injection-molded and reaction-bonded material. Mag. 3000X

Figure 3. SCANNING ELECTRON MICROGRAPHS OF DUPLEX MICROSTRUCTURES IN RBSi_3N_4 . NOTE DIFFERENCES IN WHISKER PHASE MORPHOLOGY.

The kinetics of the reaction bonding process are being investigated by various workers but as yet are not well defined. The investigations which have been carried out demonstrate that particle size and purity are extremely important.^{10,11} Iron impurities at the 1% level greatly accelerate the reaction to RBSi_3N_4 . Initial powder particle size has been shown to effect final pore size¹² and thus mechanical properties of the final material, and also influence reaction rates while forming RBSi_3N_4 .¹¹

The mechanical properties of reaction-bonded silicon nitride are also rather interesting. Material with approximately 20% porosity has been obtained with reported bend strengths of 43,000 psi (c. 300 MN/m²). Since fully dense hot-pressed Si_3N_4 has a bend strength of about 115,000 psi (c. 800 MN/m²), the relatively high bend strength of the reaction-bonded material with 20% porosity is unusual. One may speculate that the answer may lie with the duplex microstructure. There may be some reinforcement of the material by the in situ formed α Si_3N_4 whiskers. If this should prove to be the case, a new class of composite materials may be considered "autocomposites". However, much work needs to be done to elucidate the structure/property relationships in this material.

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